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Elimination of sulfaclozine from water with $SO_4^{\bullet-}$ radicals: Evaluation of different persulfate activation methods

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ABSTRACT

The evaluation of different persulfate activation methods (UV, solar light, electron, Fe(II)) on the degradation of sulfaclozine was investigated along with the effect of persulfate concentrations. UV/TiO_2/$K_2S_2O_8$ resulted in the highest degradation rate regardless persulfate concentrations. However, persulfate addition on the UV/TiO_2 system was not as efficient as expected and the use of radical scavengers showed that pH played an important role in the distribution of dominant radicals. It was found that at pH 7, hydroxyl and sulfate radicals were involved in the degradation of sulfaclozine, whereas at pH 11 no contribution of sulfate radicals was observed.

Following the formation of the six by-products of the first generation formed in UV/TiO_2 system, we obtained the formation of two by-products out of six in the UV/$K_2S_2O_8$ system and four in the UV/TiO_2/$K_2S_2O_8$ system but with different concentrations, confirming the hypothesis suggested about the intervention of $O_2^{\bullet-}$ in the degradation mechanism of sulfaclozine.

The second order rate constant of the reaction between sulfaclozine and $SO_4^{\bullet-}$ radicals was determined by a competitive kinetics method and two values of 7.5×10^9 M^{-1} s^{-1} and 1.7×10^{10} M^{-1} s^{-1} were obtained depending on the references used, and found to be close to those obtained between sulfaclozine and $^{\bullet}OH$ radicals (7.2×10^9 M^{-1} s^{-1} and 5.9×10^9 M^{-1} s^{-1}).

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1. Introduction

Sulfaclozine is a sulfonamide antibiotic (Fig. 1) widely used for the treatment of various poultry diseases. This antibiotic used in veterinary treatments is weakly absorbed from the gastrointestinal tract of animals and then, can be excreted intact in the environment and discharged into water cycles [1].

Furthermore, conventional wastewater treatment plants using biological treatments are not well adapted for removing biologically active molecules such as sulfonamide antibiotics [2–4] and therefore additional treatments such as the AOPs (Advanced Oxidation Processes) are often required [5,6].

In-situ chemical oxidation (ISCO) is an efficient technique used for the ground water remediation [7,8] involving the use of oxidants to remove organic pollutants from water. Several oxidants can be used for ISCO, but the main four are: persulfate, permanganate, hydrogen peroxide and ozone [7,9].

Recently, persulfate has also received attention for water remediation due to its high stability, aqueous solubility, high efficiency and relatively low cost [10,11]. Persulfate is a strong oxidant ($E^0(S_2O_8^{2-}/SO_4^{2-}) = 2.05$ V/ENH) [12] and can act directly as an oxidant but its rate of contaminants oxidation remains limited. In order to enhance its efficiency, persulfate has to be activated to generate more powerful sulfate radicals ($SO_4^{\bullet-}$). In this context, heat, UV, electron and transition metals (e.g., ferrous ion (Fe(II)) [12–16] were used.

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\bullet-} \quad (1)$$

$$S_2O_8^{2-} + h\upsilon \rightarrow 2SO_4^{\bullet-} \quad (2)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} \quad (3)$$

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + M^{(n+1)+} \quad (4)$$

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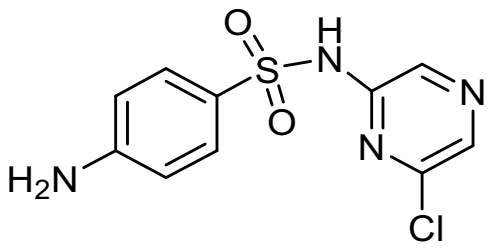

Fig. 1. Organic structure of sulfaclozine.

$SO_4^{\bullet-}$ radical is a stronger oxidant than persulfate ion ($E^0(SO_4^{\bullet-}/SO_4^{2-}) = 2.6$ V/ENH) [13,17] and has a high efficiency in the mineralization of organic pollutants. Moreover, it is efficient in removing halogen-substituted pollutants [18]. $SO_4^{\bullet-}$ engages at least three reaction modes with organic compounds: (i) by hydrogen abstraction from saturated carbon, (ii) by addition on a double bond and (iii) by electron transfer. Noting that the latter mechanism is not feasible by •OH radicals with uncharged species [16]. Persulfate can also be activated by TiO_2 photocatalytic system by trapping the photogenerated electrons in the conduction band, Eq. (3). In this latter case the photocatalytic degradation should be enhanced due to the fact that the e^-/h^+ recombination rate will be reduced, further radical species will be present in the solution and some sulfate radicals could be turned into hydroxyl radicals Eq. (5) [13,19]:

$$SO_4^{\bullet-} + H_2O \rightarrow {}^{\bullet}OH + SO_4^{2-} + H^+ \quad (5)$$

The rate-enhancing effect of adding $K_2S_2O_8$ to UV/TiO_2 system was clearly confirmed, for example, for pentachlorophenol [13], azo dyes [19], trichloroethylene [20] and imazalil [16].

It is well known that pH plays a very important role in the distribution of dominant radicals involved in the degradation mechanism [21]. In fact, $SO_4^{\bullet-}$ reacts with HO^- to form •OH radicals with a rate constant of 6.5×10^7 M^{-1} s^{-1} under alkaline conditions according to the following reaction [22]:

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \quad (6)$$

Thus, to determine the radicals most involved in the degradation mechanism, radical scavengers such as alcohol can be used. *Tert*–butanol can be used to scavenge mainly hydroxyl radicals ($k^{\bullet}OH = 5.2 \times 10^8$ M^{-1} s^{-1}; $kSO_4^{\bullet-} = 8.4 \times 10^5$ M^{-1} s^{-1}) [23,24], while methanol can be used to scavenge both hydroxyl and sulfate radicals ($k^{\bullet}OH = 1 \times 10^9$ M^{-1} s^{-1}; $kSO_4^{\bullet-} = 1 \times 10^7$ M^{-1} s^{-1}) [24,25].

The main objectives of this study were: (1) to determine the rate constant of the reaction between sulfaclozine and $SO_4^{\bullet-}$ radicals for comparison with •OH radicals, (2) to study the degradation of sulfaclozine in different systems with different activation methods of persulfate (UV, solar light, UV/TiO_2, Fe(II)), (3) to study the effect of persulfate concentration in each system, (4) to carry out experiments at different pHs with and without scavengers in the UV/TiO_2/$K_2S_2O_8$ system to find out the most involved radicals in the degradation mechanism, and (5) to compare the by-products identified by LC–MS/MS in UV/TiO_2, UV/$K_2S_2O_8$ and UV/TiO_2/$K_2S_2O_8$ systems.

2. Materials and methods

2.1. Chemicals and reagents

Sulfaclozine sodium (99% purity) was purchased from Sigma-Aldrich and used as received. Titanium dioxide AEROXIDE TiO_2 P 25 was provided by Evonik Degussa with a specific BET area of 50 m^2 g^{-1}, a mean particle size of 30 nm and crystal distribution of 80% anatase and 20% rutile (properties were given for the suppliers). Polyvinylidene fluoride PVDF filters (0.45 μm) were purchased from Millipore. Iron(II) sulfate, acetonitrile, NaOH, formic acid, potassium persulfate ($K_2S_2O_8$), methanol (LC–MS/MS grade) and *tert*-butanol were purchased from Sigma-Aldrich. Ultra pure water was obtained from a Millipore Waters Milli-Q water purification system. Other reagents were at least of analytical grade.

2.2. Experimental procedure

2.2.1. UV/TiO_2, UV/$K_2S_2O_8$ and UV/TiO_2/$K_2S_2O_8$ systems

Experiments were performed in an open Pyrex glass reactor (cut-off at 295 nm) with an inner diameter of 4 cm and height of 9 cm with a double walled cooling water jacket to keep the temperature of the solutions constant throughout the experiments (20 °C). An HPK 125 W Philips water cooled mercury lamp with a maximum emission wavelength of 365 nm and in a lower emission wavelength of 312 nm, was used as a light source. The radiant flux entering the irradiation cell was measured by a VLX-3W radiometer with a CX-365 detector (UV-A) and a value of 4 mW cm^{-2} was found at the walls of the reactor. Adequate persulfate doses were added into 25 mL of sulfaclozine solution (88 μmol L^{-1}) and the reaction solution was mixed by a magnetic stirrer to ensure homogeneity during the reaction. When needed, 2.5 g L^{-1} of TiO_2 was added 20 min before irradiation to reach the adsorption-desorption equilibrium. To investigate the role of hydroxyl and sulfate radicals in the degradation of sulfaclozine, methanol and/or *tert*–butanol were added at the beginning of the experiments. The pH value (pH 11) was adjusted by adding concentrated solution of NaOH in the sulfaclozine solution. The first sample was taken out at the end of the dark adsorption period just before turning on the irradiation, in order to determine the bulk sulfaclozine concentration. This value was taken as the initial concentration for the photocatalytic experiment. During irradiation, the samples were with-drawn regularly from the reactor and filtered immediately through 0.45 μm PVDF membrane filters to remove TiO_2 particles.

2.2.2. Solar light/$K_2S_2O_8$ system

The degradation of 50 mL of sulfaclozine solution (88 μmol L^{-1}) was carried out in a Pyrex reactor equipped with a solar light simulator (Suntest CPS+, Heraeus) and a 1.1 kW Xenon arc lamp. The solution was stirred with a magnetic stirrer bar and adequate persulfate doses were added just before the irradiation.

2.2.3. Fe(II)/$K_2S_2O_8$ system

Experiments were performed in a conical flask under mechanical stirring at room temperature (20 °C). Adequate persulfate and Fe(II) doses were added into 50 mL of sulfaclozine solution (88 μmol L^{-1}). The reaction solution was mixed by a magnetic stirrer to ensure homogeneity during the reaction. It is noteworthy that although Fenton and Fenton-like systems are more efficient at pH > around 3 (at pH □ 4 ferric ions precipitate as ferric hydroxide $Fe(OH)_3$ which is very stable ($Ks = 10^{-38}$) limiting the reduction of Fe(III) to Fe(II) and the regeneration of Fe(II)), we have worked in this study at pH 7 since sulfaclozine is rapidly hydrolyzed at acidic pH [26].

It should be noted that, in these systems, control experiments were carried out and the removal of the substrate was considered negligible and that the most of the measurements were repeated up to 3 times and the error for those repeated were less than 5%

2.3. Analytical methods

2.3.1. HPLC-DAD

The concentration of sulfaclozine during the degradation was determined using Shimadzu VP series HPLC system equipped with a

photodiode array detector (PDA). A 20 μL of filtered irradiated samples (25 mg L^{-1}) was directly injected. Analytical separation was performed using an Interchim C18 column (125 mm × 4 mm, particle size 5 μm) with a mobile phase of 80% water at pH 3 (adjusted with formic acid) and 20% ACN at a flow rate of 0.5 mL min^{-1}. The detection wavelength was 271 nm, corresponding to λ_{max} of sulfaclozine at pH 3.

2.3.2. LC–MS/MS

The appearance and disappearance of the different intermediates already identified in a previous study on the photocatalytic degradation of sulfaclozine on TiO_2 suspensions [26] were analyzed using LC–MS/MS in SIM mode. Therefore, aliquots were taken at regular time intervals during irradiation and after filtration to separate the TiO_2 particles when necessary.

The LC system was interfaced to an Agilent 6410 triple quadrupole mass spectrometer (Agilent technologies, USA) via electrospray ionization (ESI) source and operated in positive mode using high purity nitrogen gas as a collision gas and also as nebulization gas at 30 and 40 psi respectively. The source temperature was maintained at 350 °C. The separation was performed with a DIONEX C18 column (250 mm × 4.6 mm, particle size 5 μm) with a mobile phase of 80% water at pH 3 (adjusted with formic acid) and 20% ACN at a flow rate of 0.7 mL min^{-1}.

2.4. Determination of the second-order rate constant of sulfaclozine reaction with $SO_4^{\bullet-}$ radicals

Competition kinetics were used to determine the second order rate constant between sulfaclozine and sulfate radicals $k(SO_4^{\bullet-},SCL)$. Solar light simulator was used to activate persulfate (17.6 mmol L^{-1}) and generate sulfate radicals. Benzoic acid (BA), for which its rate constants with •OH and $SO_4^{\bullet-}$ are known to be respectively $k(^{\bullet}OH,BA) = 5.9 \times 10^9\ M^{-1}s^{-1}$ [23,27] and $k(SO_4^{\bullet-},BA) = 1.2 \times 10^9\ M^{-1}s^{-1}$ [15] was used as a reference in this study. However, since at pH 7 the sulfate radical can react with H_2O and OH^- to generate •OH radicals according to the Eq. (5) and Eq. (6) respectively, both radicals can be responsible for the degradation of the compounds. Thus, nitrobenzene (NB) which reacts very slowly with sulfate radicals [15,28] was added together with benzoic acid to calculate the degradation due to •OH radicals ($k(^{\bullet}OH,NB) = 3.9 \times 10^9\ M^{-1}s^{-1}$) [23]. The rate constant between •OH and sulfaclozine was already calculated in a previous study and a value of $k(^{\bullet}OH,SCL) = 7.2 \times 10^9\ M^{-1}\ s^{-1}$ had been found [26]. Equimolar solution of sulfaclozine, BA and NB (88 μmol L^{-1}) was oxidized and the concentrations of the three compounds were monitored using HPLC-DAD at the same conditions (λ_{max}BA = 230 nm and λ_{max}NB = 266 nm).

3. Results and discussion

3.1. Determination of the second-order rate constant of sulfaclozine reacting with $SO_4^{\bullet-}$ radicals

The degradation of SCL can be described by the following reactions. Noting that the direct photolysis of SCL, NB and BA were considered as negligible (less than 4%) and steady state concentrations were supposed for hydroxyl and sulfate radicals.

$$(d[SCL])/dt = k(^{\bullet}OH, SCL)[^{\bullet}OH][SCL] + k(SO_4^{\bullet-}, SCL)[SO_4^{\bullet-}][SCL]; \quad (7)$$

$$\ln([SCL]0/[SCL]t) = (k(^{\bullet}OH, SCL) \times [^{\bullet}OH] + k(SO_4^{\bullet-}, SCL) \times [SO_4^{\bullet-}]) \times t$$

$$(d[NB])/dt = k(^{\bullet}OH, NB)[^{\bullet}OH][NB]; \quad (8)$$

$$\ln([NB]0/[NB]t) = (k(^{\bullet}OH, NB) \times [^{\bullet}OH]) \times t$$

$$(d[BA])/dt = k(^{\bullet}OH, BA)[^{\bullet}OH][BA] + k(SO_4^{\bullet-}, BA)[SO_4^{\bullet-}][BA]; \quad (9)$$

$$\ln([BA]0/[BA]t) = (k(^{\bullet}OH, BA) \times [^{\bullet}OH] + k(SO_4^{\bullet-}, BA) \times [SO_4^{\bullet-}]) \times t$$

By calculating [•OH] and $[SO_4^{\bullet-}]$ from Eqs. (8) and (9) respectively, and applying the obtained values to Eq. (7), the second-order rate constant of sulfaclozine with sulfate radicals was calculated and a value of $1.7 \times 10^{10}\ M^{-1}\ s^{-1}$ was found which is very high and not very different from that obtained with •OH radicals ($7.2 \times 10^9\ M^{-1}\ s^{-1}$) [26]. It is noteworthy that this value depends as well on the other kinetic rate constants used as references for its determination. For example, here we have used a value for $k(^{\bullet}OH,BA)$ of $5.9 \times 10^9\ M^{-1}\ s^{-1}$ [23,27], while other authors proposed different values. For example, Liang et al. suggest a value for $k(^{\bullet}OH,BA)$ of $4.2 \times 10^9\ M^{-1}\ s^{-1}$ [21]. By choosing this new value for $k(^{\bullet}OH,BA)$ we obtain for $k(^{\bullet}OH,SCL)$ a value of $5.9 \times 10^9\ M^{-1}\ s^{-1}$ and for $k(SO_4^{\bullet-},SCL)$ a value of $7.5 \times 10^9\ M^{-1}\ s^{-1}$. This value remains high and comparable with the ones proposed for other sulfonamides. For example, the second-order rate constant between $SO_4^{\bullet-}$ and sulfamethoxazole (another sulfonamide) was reported to be $1.2 \times 10^{10}\ M^{-1}\ s^{-1}$ by Ahmed et al. [6] and $(1.61 \pm 0.17) \times 10^{10}\ M^{-1}\ s^{-1}$ by Zhang et al. [28]. All these values are comparable since $SO_4^{\bullet-}$ radicals prefer to attack the aniline moiety, common for all sulfonamides. Indeed, $SO_4^{\bullet-}$ radical is a highly selective electrophile mainly acting by electron-transfer from N to $SO_4^{\bullet-}$ yielding to a N-centered radical as the first intermediate [28,29].

3.2. Oxidation of sulfaclozine with UV-activated persulfate

Persulfate irradiated with UV is assumed to generate $SO_4^{\bullet-}$ through Eq. (2). In this process •OH radicals are not produced directly but can be generated when $SO_4^{\bullet-}$ reacts with water or with $^-$OH in alkaline conditions according to Eqs. (5) and (6) respectively. Fig. 2 presents the effect of $K_2S_2O_8$ on sulfaclozine degradation at pH 7. The figure shows that the degradation rate of sulfaclozine increased in line with the increasing $[K_2S_2O_8]/[SCL]$ ratio from 20 to 500.

The plot of ln (C_0/C) versus irradiation time yields a linear relationship indicating a pseudo-first order reaction and values for the rate constants of 2×10^{-3}, 9×10^{-3}, 21×10^{-3}, 53×10^{-3} min^{-1} were found for the ratio $[K_2S_2O_8]/[SCL]$ of 20, 100, 200, 500, respectively. In addition, these pseudo-first constant rates showed proportional relationship with the initial concentrations of persulfate (see the inset of Fig. 2).

It is noteworthy that persulfate can be activated by photons whose wavelengths are comprised between 193 and 351 nm. Hence, even though the main emitted wavelength from HPK lamp at 365 nm cannot activate persulfate, the one at 312 nm with a lower intensity can efficiently activate it with a sufficiently high quantum yield ($\Phi = 1.1$) [30].

3.3. Oxidation of sulfaclozine with solar light-activated persulfate

Fig. 3 shows that the use of solar simulator allows the degradation of sulfaclozine at pH 7 and here also the rate of the degradation increased in line with $[K_2S_2O_8]/[SCL]$ ratio from 20 to 500 (initial concentration of sulfaclozine = 88 μM) since more sulfate radicals can be generated. With $[K_2S_2O_8]/[SCL] = 500$, a total elimination of sulfaclozine was reached after 30 min of irradiation. These results showed that persulfate is efficiently activated with solar light irradiation.

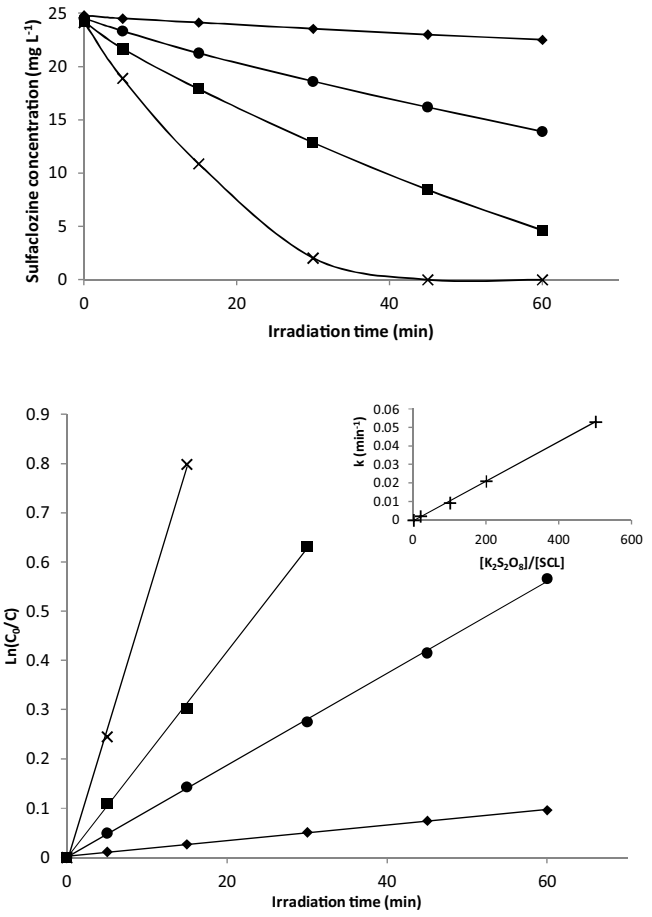

Fig. 2. Effect of the concentration of $K_2S_2O_8$ on sulfaclozine degradation in UV/$K_2S_2O_8$ system (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}), initial pH = 7). (♦) [$K_2S_2O_8$]/[SCL] = 20; (●) [$K_2S_2O_8$]/[SCL] = 100; (■) [$K_2S_2O_8$]/[SCL] = 200; (×) [$K_2S_2O_8$]/[SCL] = 500.

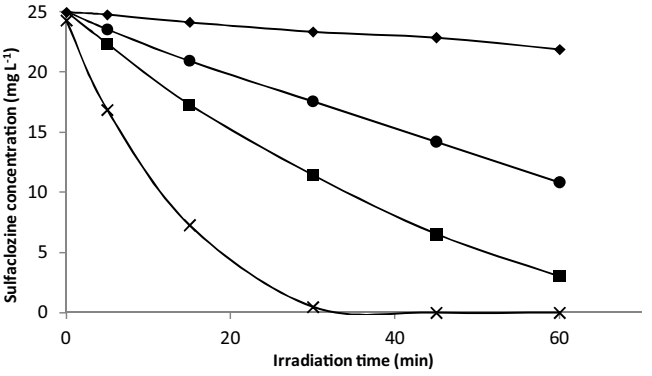

Fig. 3. Effect of $K_2S_2O_8$ concentrations on sulfaclozine degradation by Solar light/$K_2S_2O_8$ system (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}), initial pH = 7). (♦) [$K_2S_2O_8$]/[SCL] = 20; (●) [$K_2S_2O_8$]/[SCL] = 100; (■) [$K_2S_2O_8$]/[SCL] = 200; (×) [$K_2S_2O_8$]/[SCL] = 500.

3.4. Oxidation of sulfaclozine with Fe(II)-activated persulfate

Among the different transition metals, ferrous ions Fe(II) are the most commonly used for persulfate activation. The reactions between persulfate and Fe(II) are expressed by the following equations [7,31–33]:

$$Fe(II) + S_2O_8^{2-} \rightarrow Fe(III) + SO_4^{2-} + SO_4^{\bullet-}; k = 2.7 \times 10^1\ M^{-1}\ s^{-1} \quad (10)$$

$$Fe(II) + SO_4^{\bullet-} \rightarrow Fe(III) + SO_4^{2-} k = 4.6 \times 10^9\ M^{-1}\ s^{-1} \quad (11)$$

The overall reaction from Eq. (10) and (11) gives:

$$2Fe(II) + S_2O_8^{2-} \rightarrow 2Fe(III) + 2SO_4^{2-}; k = 3.1 \times 10^4\ M^{-1}\ s^{-1} \quad (12)$$

3.4.1. Effect of Fe(II) concentration

The effect of the initial Fe(II) concentration on the degradation of 88 μmol L^{-1} solution of sulfaclozine in the Fe(II)/$K_2S_2O_8$ system ([$K_2S_2O_8$]/[SCL] = 200) at pH 7 was investigated as shown in Fig. 4. Five different concentrations of Fe(II) (0.2, 0.5, 1, 2 and 4 mM) were used. An increasing concentration of Fe(II) from 0.2 to 1 mM led to the enhancement of the degradation rate of sulfaclozine. The greater efficiency of sulfaclozine degradation at the higher Fe(II) dose resulted from the higher production of $SO_4^{\bullet-}$ radicals in the reaction. The degradation rate did not change when the initial concentration of Fe(II) increased from 1 mM to 2 mM and decreased when the initial concentration was higher than 2 mM. In fact, a too high amount of Fe(II) might scavenge $SO_4^{\bullet-}$ radicals according to the Eq. (11).

A similar phenomenon was reported by Liang et al. [31], Zhou et al. [34] and Romero et al. [35] for the degradation of organic compounds by ferrous-activated persulfate. It is noteworthy that the rapid conversion of Fe(II) to Fe(III) can be a reason for the limited oxidizing capability of the system [31] which can explain the shape of the degradation curve in Figs. 4 and 5. The effect of adding chelating agents to the system can be interesting for a subsequent study.

3.4.2. Effect of persulfate concentration

Four different molar ratios of persulfate/[sulfaclozine] ([$K_2S_2O_8$]/[SCL] = 20, 100, 200 and 500) activated with 1 mM Fe(II) were employed in the experiments to investigate the influence of persulfate concentration on sulfaclozine degradation. Fig. 5 shows that the increase of [$K_2S_2O_8$]/[sulfaclozine] ratio from 20 to 200 accelerated the oxidation of sulfaclozine. The initial rate of the reaction was found to be 1.1, 1.3 and 1.8 mol L^{-1} min^{-1} when [$K_2S_2O_8$]/[SCL] = 20, 100, 200 respectively. For the higher persulfate concentration ([$K_2S_2O_8$]/[sulfaclozine] = 500) no enhancement of sulfaclozine degradation was observed which can be ascribed to the reaction between Fe(II) and the excessive persulfate concentration according to Eq. (12).

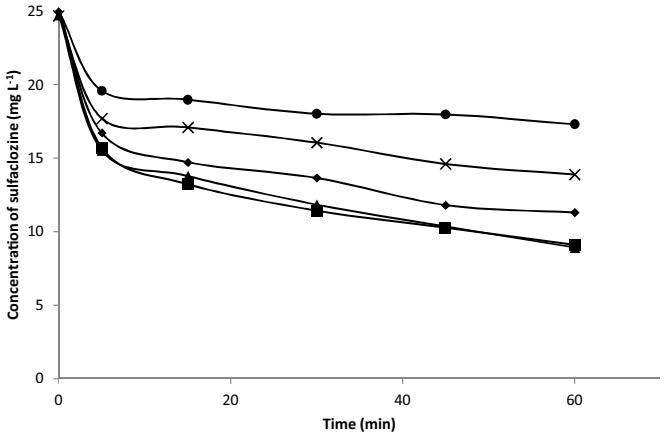

Fig. 4. Effect of the amount of Fe(II) on sulfaclozine degradation by Fe(II)/$K_2S_2O_8$ system (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}), [$K_2S_2O_8$]/[SCL] = 200, initial pH = 7). (●) [Fe(II)] = 0.2 mM; (×) [Fe(II)] = 0.5 mM; (▲) [Fe(II)] = 1 mM; (■) [Fe(II)] = 2 mM; (♦) [Fe(II)] = 4 mM.

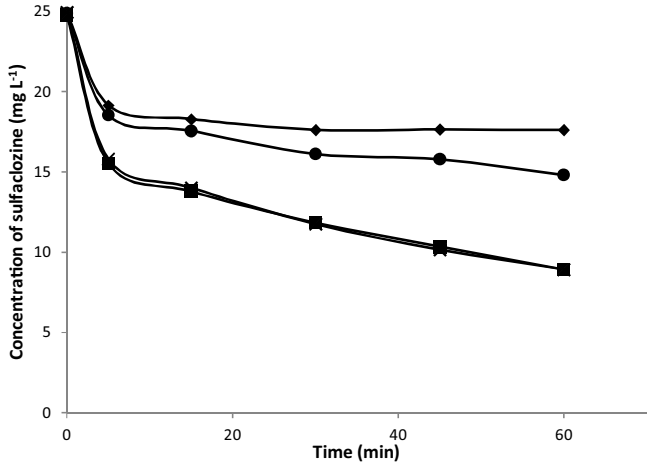

Fig. 5. Effect of $K_2S_2O_8$ concentration on sulfaclozine degradation in Fe(II)/$K_2S_2O_8$ system (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}), [Fe(II)] = 1 mM, initial pH = 7). (♦) [$K_2S_2O_8$]/[SCL] = 20; (●) [$K_2S_2O_8$]/[SCL] = 100; (■) [$K_2S_2O_8$]/[SCL] = 200; (×) [$K_2S_2O_8$]/[SCL] = 500.

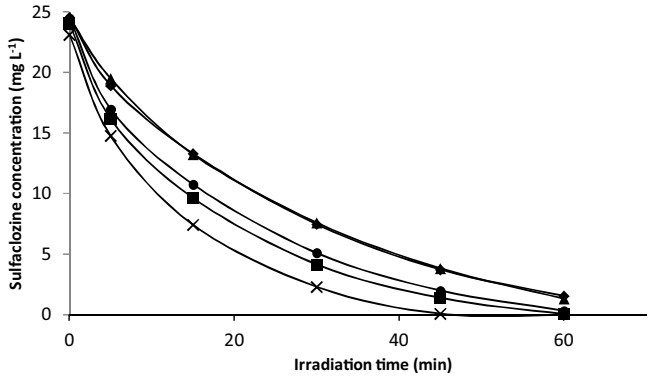

Fig. 6. Effect of $K_2S_2O_8$ concentration on sulfaclozine degradation by UV/TiO_2/$K_2S_2O_8$ system (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}), TiO_2 dose = 2.5 g L^{-1}, initial pH = 7). (▲) [$K_2S_2O_8$]/[SCL] = 0; (♦) [$K_2S_2O_8$]/[SCL] = 20; (●) [$K_2S_2O_8$]/[SCL] = 100; (■) [$K_2S_2O_8$]/[SCL] = 200; (×) [$K_2S_2O_8$]/[SCL] = 500.

3.5. Oxidation of sulfaclozine with UV/TiO_2-activated persulfate

3.5.1. Effect of persulfate concentration

Persulfate is assumed to highly enhance the photocatalytic degradation process by reducing the probability of the recombination of photogenerated electrons and holes and by forming reactive radicals that can enter in the photocatalytic process [16,36,37]. The effect of the addition of $S_2O_8^{2-}$ on TiO_2 photocatalysis of sulfaclozine at pH 7 was illustrated in Fig. 6, and it was found that the rate of the photocatalytic degradation increased with the increasing amount of $S_2O_8^{2-}$. From the curves, the first-order rate constants for the degradation of sulfaclozine with [$K_2S_2O_8$]/[SCL] = 0, 20, 100, 200, 500 were determined and values of 3.9×10^{-2}, 4.5×10^{-2}, 5.4×10^{-2}, 6.2×10^{-2} and 7.6×10^{-2} min^{-1} respectively, were obtained. However, the rate enhancement was not as high as it was expected. Indeed, in a previous study about the degradation of sulfaclozine on TiO_2 suspensions, it was assumed that the conduction-band electrons could intervene in the degradation of sulfaclozine either directly or by the formation of superoxide radicals [26] which can explain why we did not get a high enhancement. Moreover Mezyk et al. suggested that the reaction of sulfa drugs with hydrated electron is very rapid ($k = 2.0 \times 10^{10}$ M^{-1} s^{-1}) [38]. In other words, there is a competition between SCL, $S_2O_8^{2-}$ and O_2 towards the conduction-band electrons as shown in the following reactions with:

$$S_2O_8^{2-} + e^-_{CB} \rightarrow SO_4^{2-} + SO_4^{\bullet -} \quad (3)$$

$$SCL + e^-_{CB} \rightarrow \text{By-products} \quad (13)$$

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet -} \quad (14)$$

As a result, the main role usually played by persulfate to scavenge electrons may not have a great effect in our case. Thus, the main effect here of adding persulfate should be the generation, by UV, of other reactive species such as $SO_4^{\bullet -}$ radicals. The effect of persulfate addition on the formation of the first generation products in different systems can provide important information (part 3.7).

3.5.2. Effect of tert-butanol and methanol on the degradation of sulfaclozine in the UV/TiO_2/$K_2S_2O_8$ system

In this study, experiments using methanol and *tert*-butanol in the UV/TiO_2/$K_2S_2O_8$ system were performed at pH 7 and pH 11 (Fig. 7);

[sulfaclozine] = 88 μmol L^{-1},

[TiO_2] = 2.5 g L^{-1}, [$K_2S_2O_8$]/[sulfaclozine] = 100, [alcohol]/[sulfaclozine] = 500.

Fig. 7 shows that at pH 7 the rate of inhibition obtained with both alcohols are different, since with methanol this rate represented c.a. 70% of the initial rate of reaction and c.a. 34% with *tert*-butanol. This result allows us to conclude that both •OH and $SO_4^{\bullet -}$ radicals contributed in the degradation of sulfaclozine.

However, at pH 11 the same percentage of inhibition was obtained with both alcohols, meaning that at this pH, sulfate radicals are not involved in the degradation of sulfaclozine.

3.6. Effect of pH

It was found that pH can play a role in the distribution of dominant radicals involved in the degradation of sulfaclozine. In this context, the degradation of sulfaclozine was performed at pH 7 and pH 11 and the results are as shown in Fig. 8. It is noteworthy that at acidic pH a comparison could not be accurate due to a fast sulfaclozine hydrolysis [26].

The results shows that:

1) For the UV/TiO_2 system, the degradation rate of sulfaclozine at pH 11 was higher than that at pH 7 which can be explained by the fact that (i) at basic pH, there is an increase of •OH concentration according to the following reaction:

$$OH^- + h^+ \rightarrow {}^{\bullet}OH \quad (15)$$

(ii) the size of aggregates formed by TiO_2 is smaller at pH 11 than that at pH 7 [39] and therefore the surface will be higher.

However, the adsorption of sulfaclozine molecules on TiO_2 at pH 7 was low (5%) [26] and its adsorption was negligible at pH 11 allowing us to eliminate this hypothesis.

2) For the UV/$K_2S_2O_8$ system, the rate constants at pH 7 and pH 11 were almost the same, meaning that pH does not play an important role in this case. Hazime et al. [16] and Lin et al. [40] found the same results for the degradation of imazalil and phenol respectively. These results can be explained by the fact that no matter how the distribution between •OH and SO_4^{-}radicals is, the same degradation rate should be obtained since k(•OH,SCL) and k(SO_4^{-},SCL) are found to be close.
3) For the UV/TiO_2/$K_2S_2O_8$ system, the rate constant at pH 11 was greater than that obtained at pH 7 for the same reasons given for the UV/TiO_2 system.

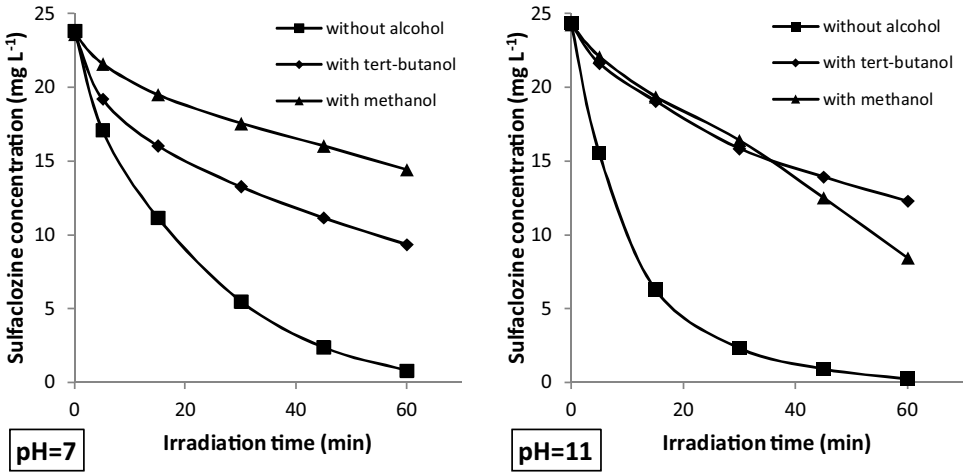

Fig. 7. Effect of methanol and *tert*-butanol on the degradation of sulfaclozine at pH 7 and pH 11 in UV/TiO_2/$K_2S_2O_8$ system (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}), TiO_2 dose = 2.5 g L^{-1}, $[K_2S_2O_8]$/[SCL] = 100, [*alcohol*]/[SCL] = 500).

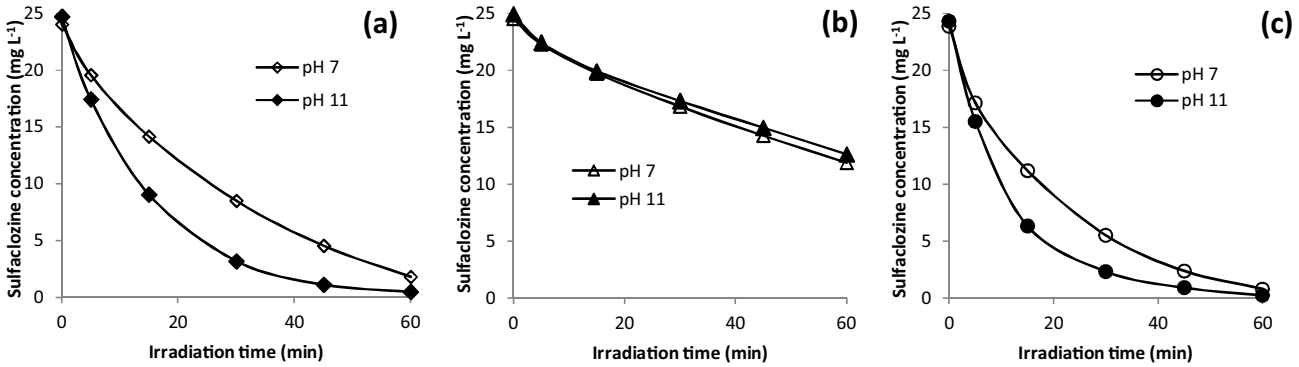

Fig. 8. Effect of pH on sulfaclozine degradation in three systems: (a) UV/TiO_2, (b) UV/$K_2S_2O_8$, and (c) UV/TiO_2/$K_2S_2O_8$ (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}), TiO_2 dose = 2.5 g L^{-1}, $[K_2S_2O_8]$/[SCL] = 100).

3.7. Monitoring by-products formation by LC–MS/MS

Since different radicals are present in the system at pH 7 it is significant to compare the formation of by-products in UV/TiO_2, UV/$K_2S_2O_8$ and UV/TiO_2/$K_2S_2O_8$ systems. It is also noteworthy that the same by-products could be obtained but with different pathways. The percentage of the formation of the 6 by-products of the first generation already identified in a previous study [26] were presented in Fig. 9. The abundance of these products after the conversion of 50% of sulfaclozine initial concentration in UV/$K_2S_2O_8$ and UV/TiO_2/$K_2S_2O_8$ systems was presented by reference to their abundance in the UV/TiO_2 system.

By-products 1 and 3 with $[MH^+]$ = 110 and 174 respectively were not formed in the UV/$K_2S_2O_8$ system which is in agreement with the fact that $O_2^{\bullet-}$ radicals were found to be the responsible species for the formation of these products [26]. In fact, in the absence of TiO_2 there is no generation of electrons and thus there is no formation of $O_2^{\bullet-}$ radicals according to the following reactions:

$$TiO_2 + h\upsilon \rightarrow e^- + h^+ \quad (16)$$

$$O_2 + e^- \rightarrow O_2^{\bullet-} \quad (14)$$

In the UV/TiO_2/$K_2S_2O_8$ system, product 1 was not formed and only 35% of product 3 was formed. This decrease in its abundance can be explained by the competition between sulfaclozine, persulfate and O_2 towards the conduction band electrons according to Eqs. (3), (13) and (14).

Different pathways were assumed for the formation of the by-product 2 for the three systems. Concerning the UV/TiO_2 system, it was suggested in a previous study, that the conduction-band electrons were the responsible species for the formation of this product. But a higher formation rate of this by-product was observed after the addition of persulfate and its formation was not negligible in the UV/$K_2S_2O_8$ system without TiO_2 and valence-band electrons. Indeed, Ahmed et al. and Ji et al. [6,41] also found the same cleavage of the sulfonamide bonds induced by sulfate radicals attack on nitrogen.

In the UV/$K_2S_2O_8$ and UV/TiO_2/$K_2S_2O_8$ systems, by-product 4 with $[MH^+]$ = 195 was not formed since, in the UV/TiO_2 system, this product was formed by an electrophilic addition of •OH radicals to the aromatic ring. Indeed, hydroxyl and sulfate radicals do not react similarly with sulfaclozine: •OH prefer to react with the molecule through hydrogen abstraction or through addition on the double bond while $SO_4^{\bullet-}$ prefer to react with the molecule by electron transfer [15,22].

In the UV/TiO_2/$K_2S_2O_8$ system, both by-products 5 and 6 with $[MH^+]$ = 301 were formed with an abundance similar to that obtained in the UV/TiO_2 system (97% and 88% respectively), whereas in the UV/$K_2S_2O_8$ system only by-product 5 was formed. It was assumed that the formation of these two products resulted from an addition of •OH radical to the aromatic ring. However, the sulfate radical reacts with sulfaclozine by addition to the aniline ring leading to the formation of carbon-centered radicals via electron transfer from the organic compound to the sulfate radical, prior to the formation of hydroxylated products. The addition of sulfate

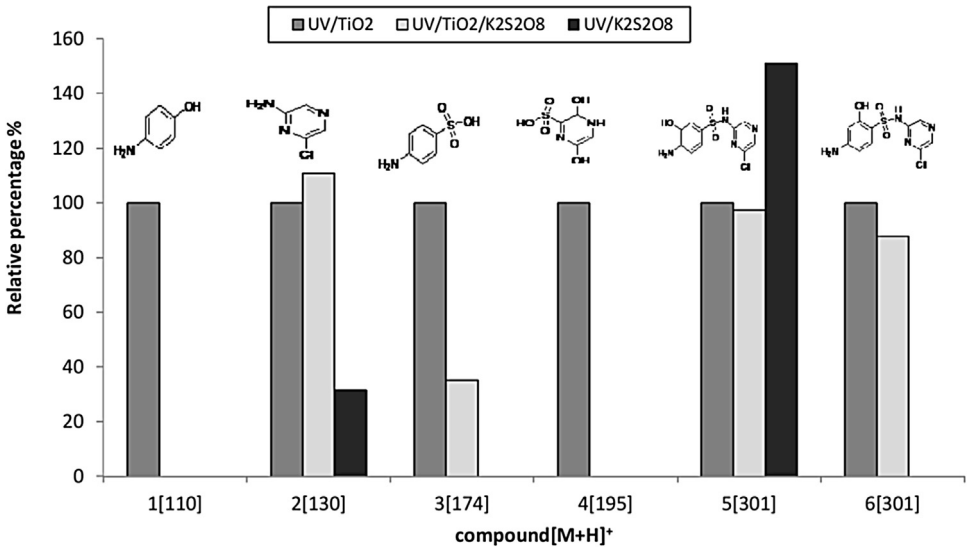

Fig. 9. Relative percentage of photoproducts formed after 50% conversion of the initial concentration of sulfaclozine in UV/TiO_2/$K_2S_2O_8$ and UV/$K_2S_2O_8$ systems compared to the UV/TiO_2 system.

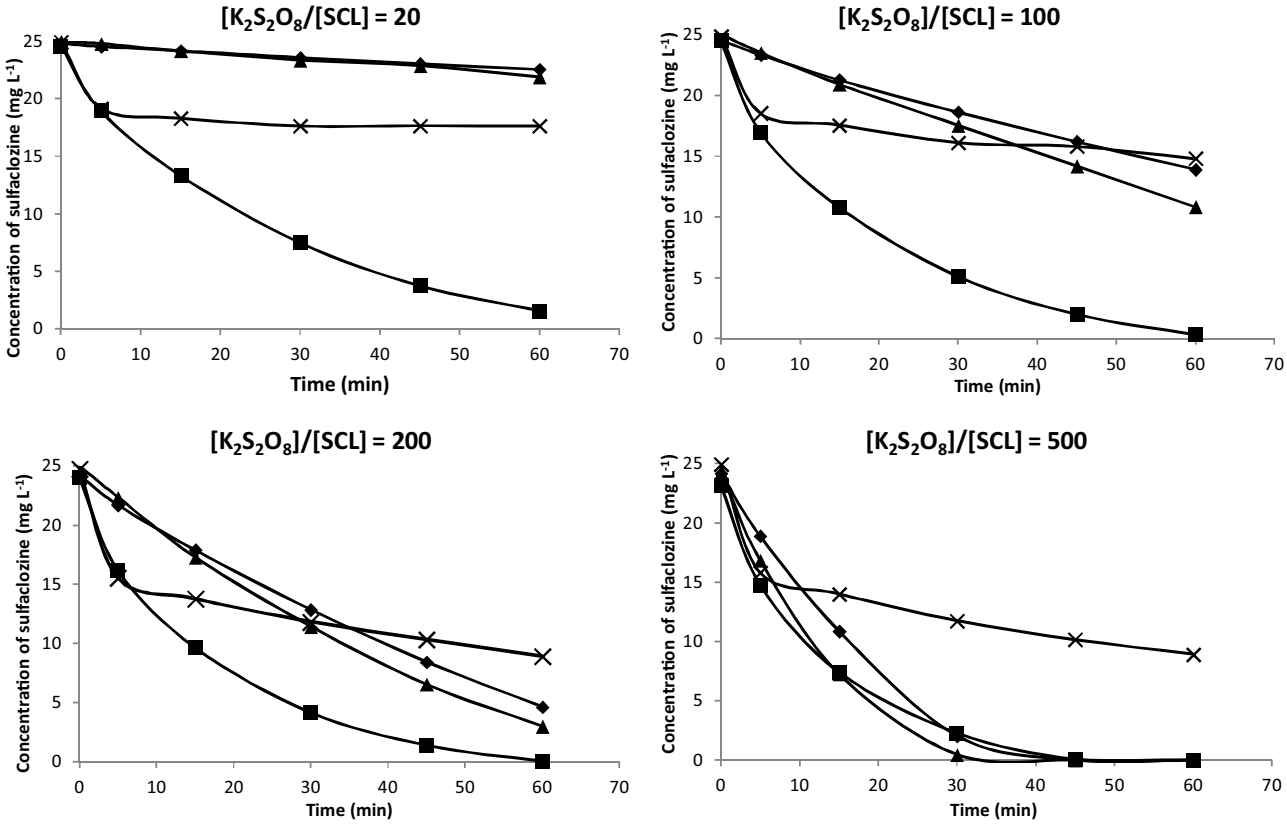

Fig. 10. Comparison of the degradation of sulfaclozine in: (♦) UV/$K_2S_2O_8$; (■) UV/TiO_2/$K_2S_2O_8$; (▲) solar light/$K_2S_2O_8$ and (×) Fe(II)/$K_2S_2O_8$ (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}), [Fe(II)] = 1 mM, TiO_2 dose = 2.5 g L^{-1}, initial pH = 7).

radicals in the *ortho* position to $-SO_2-$ group may be difficult due to steric hindrance and thus, the product 6 could not be formed with sulfate radicals. On the other hand, a new by-product with the same MW was detected in SIM mode in UV/$K_2S_2O_8$ and UV/TiO_2/$K_2S_2O_8$ systems. This compound could be obtained from the hydroxylation on the amine of aniline moiety. The same site of hydroxylation was obtained by Ahmed et al. for the degradation of sulfamethoxazole [6] and by Fan et al. for the degradation of sulfamethazine [29] with sulfate radicals.

3.8. Comparison in the different activation systems of persulfate

The sulfaclozine degradation in the UV/$K_2S_2O_8$, UV/TiO_2/$K_2S_2O_8$, solar light/$K_2S_2O_8$, and Fe(II)/$K_2S_2O_8$ systems (initial concentration of sulfaclozine = 25 mg L^{-1} (88 μmol L^{-1}),

[Fe(II)] = 1 mM, TiO_2 dose = 2.5 g L^{-1}, initial pH = 7) was compared and Fig. 10 shows results for which different $[K_2S_2O_8]$/[SCL] ratios were used. For $[K_2S_2O_8]$/[SCL] of 20, 100 and 200 the highest percentage of sulfaclozine elimination was always obtained for the UV/TiO_2/$K_2S_2O_8$ system. However, for $[K_2S_2O_8]$/[SCL] = 500 the percentage of the elimination of sulfaclozine was almost the same for the following systems: UV/$K_2S_2O_8$, UV/TiO_2/$K_2S_2O_8$, solar light/$K_2S_2O_8$ meaning that for this concentration it is not necessary to add TiO_2 since the reaction could be limited by the number of available photons. It is noteworthy that for the first 5 min, the rates of sulfaclozine degradation in UV/TiO_2/$K_2S_2O_8$ and in Fe(II)/$K_2S_2O_8$ were the same but the rapid conversion of Fe(II) to Fe(III) can be a reason for the limited oxidizing capability of the system for a longer time.

4. Conclusions

Activating persulfate ions with UV, solar irradiation, Fe(II) and UV/TiO_2 systems for $SO_4^{\bullet-}$ generation was found to be efficient for the elimination of sulfaclozine from water. The highest percentage of the elimination of sulfaclozine was obtained in the UV/TiO_2/$K_2S_2O_8$ system. It was also found that in the UV/TiO_2/$K_2S_2O_8$, at pH 7 and with $[K_2S_2O_8]$/[sulfaclozine] = 100, both hydroxyl and sulfate radicals were responsible for sulfaclozine degradation, whereas at pH 11 there was no intervention of sulfate radicals. Moreover, in the Fe(II)/UV system, both the concentrations of persulfate and Fe (II) played an important role on the degradation rate of sulfaclozine since a relatively high concentration of persulfate or Fe(II) can cause no enhancement or decrease in the degradation rate of sulfaclozine. The second-order rate constant of the reaction between sulfaclozine and $SO_4^{\bullet-}$ radicals was determined by a competitive kinetic method and two values of 7.5×10^9 M^{-1} s^{-1} and 1.7×10^{10} M^{-1} s^{-1} were found (depending on the references used), which are close to that obtained between SCL and •OH radicals. The comparison of by-products formation in the UV/TiO_2, UV/TiO_2/$K_2S_2O_8$ and UV/$K_2S_2O_8$ systems confirmed the proposed intervention of $O_2^{\bullet-}$ radicals in the degradation mechanism of sulfacolzine in the UV/TiO_2 system and showed different hydroxylation sites for •OH and $SO_4^{\bullet-}$ radicals.

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